

BAKER BOTTS LLP		EXPRESS MAIL LABEL No. EF321685794US	DATE 08 JUNE 2001
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35.U.S.C. 371		ATTORNEY'S DOCKET NO. A34350 PCT USA	
		U.S. APPLICATION NO. 09/857762	
INTERNATIONAL APPLICATION NO. PCT/KR99/00750	INTERNATIONAL FILING DATE 08 DECEMBER 1999	PRIORITY DATE CLAIMED 08 DECEMBER 1998	
TITLE OF INVENTION SEPARATOR FOR SECONDARY BATTERY AND POROUS FILM MADE OF POLYOLEFIN BLEND AND PROCESS FOR PREPARING THE SAME			
APPLICANT(S) FOR DO/EO/US Sang-Young Lee, Byeong-In Ahn, Heon-Sik Song and Myung-Man Kim			
<p>Applicant herewith submits to the United States Designated /Elected Office (DO/EO/US) the following items and other information:</p> <ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I). <input type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. <input type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). <input type="checkbox"/> has been transmitted by the International Bureau. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). <input type="checkbox"/> A copy of the International Search Report (PCT/ISA/210) <ol style="list-style-type: none"> <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). <input type="checkbox"/> have been transmitted by the International Bureau <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. <input type="checkbox"/> have not been made and will not be made. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). <p>Items 11. to 16. below concern other document(s) or information included:</p> <ol style="list-style-type: none"> <input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409) <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <input type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. <input type="checkbox"/> A substitute specification. <input type="checkbox"/> A change of power of attorney and/or address letter. <input checked="" type="checkbox"/> Other items or information: <ol style="list-style-type: none"> <input checked="" type="checkbox"/> a copy of the International Search Report (PCT/ISA/210) <input checked="" type="checkbox"/> a copy of the International Preliminary Examination Report (PCT/IPEA/409) <p>A copy of the International Publication as published WO 00/34384 (16 pages spec, 3 pages claims, abstract on first page of publication) Notification of change of Applicant PCT Request PCT/ISA/220</p>			

INTERNATIONAL APPLICATION NO. PCT/KR99/00750		INTERNATIONAL FILING DATE 08 DECEMBER 1999		PRIORITY DATE CLAIMED 08 DECEMBER 1998	
17. <input checked="" type="checkbox"/> The following fees are submitted:				CALCULATIONS <small>PTOUSE ONLY</small>	
Basic National Fee (37 CFR 1.492(a)(1)-(5): Neither international preliminary examination fee (37 CFR 1.482) Nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO (1.492(a)(3)) \$1,000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO (1.492(a)(5)) \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO (1.492(a)(2)) \$710.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) (1.492(a)(1)) \$690.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$	1,000
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 C.F.R. 1.492(e)).				\$	
Claims	Number Filed	Number Extra	Rate	\$	
Total Claims	21 -20=	1	X \$ 18.00	\$	18
Independent Claims	2 -3=	0	X \$ 80.00	\$	0
Multiple dependent claim(s) (if applicable)			+ \$270.00	\$	270
TOTAL OF ABOVE CALCULATIONS =				\$	1,288
Reduction by 1/2 for filing by small entity, if applicable.				\$	
SUBTOTAL =				\$	1,288
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				\$	
TOTAL NATIONAL FEE =				\$	1,288
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	40
TOTAL FEES ENCLOSED =				\$	1,328
				Amt. refunded	\$
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a. <input checked="" type="checkbox"/> A check in the amount of \$ 1288 & 40 to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge our Deposit Account No. 02-4377 in amount of \$ to cover the above fees. A copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-4377. A copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO: Ronald B. Hildreth BAKER BOTTS L.L.P. 30 Rockefeller Plaza New York, New York 10112-4498					
Attorney: Ronald B. Hildreth PTO Reg: 19,498 08 JUNE 2001 Date					

**SEPARATOR FOR SECONDARY BATTERY AND POROUS FILM MADE
OF POLYOLEFIN BLEND AND PROCESS FOR PREPARING THE SAME**

CROSS REFERENCE TO RELATED APPLICATION

- 5 This application is based on application No. 98-53667 filed in the Korean Industrial Property Office on December 8, 1998, the contents of which are incorporated here into by reference.

BACKGROUND OF THE INVENTION

(a) Field of the Invention

- 10 The present invention relates to a porous film made of a polyolefin blend, a process for manufacturing the same, and a separator for a secondary battery.

(b) Description of the Related Art

- 15 A battery separator basically separates the anode from the cathode, prevents a fused junction short circuit of the two electrodes, and at the same time allows the passage of an electrolyte or ions.

- 20 Although the material of a battery separator itself is inert and does not influence electrical energy storage or output, its physical properties greatly influence on the function and safety of a battery. Furthermore, even though multiple varieties of separators are currently used according to the various chemical systems and types of batteries in the field, research is still under way since special lithium secondary batteries require a separator that has different characteristics from those of separators used in the different types of conventional batteries.

- 25 The basic characteristics required in a battery separator include the provision of physical separation between the anode and the cathode, low electrical resistance for facilitating the passage of electrolyte or ions, outstanding electrolyte wettability, mechanical strength required for the

battery assembly and application, minimal separator thickness for high charging density, etc.

Particularly, the separator wettability on electrolyte directly and greatly influences productivity during battery assembly. That is, as a jelly roll is assembled by rolling up an anode, cathode, and separator and then being put into a can in which electrolyte is added, it is important that the separator wettability should be good so that electrolyte can permeate into a tightly rolled jelly roll. Therefore, increasing the permeation rate of an electrolyte by providing a hydrophilic property to a hydrophobic separator is an important issue in the battery field.

Besides the above basic characteristics, when the separator during battery assembly directly contacts the anode or the cathode which may have a rough surface, or when dendrites are formed inside a battery as the battery undergoes repeated charges and discharges in practical battery applications, scars may be formed on the separator that can result in a short circuit. The puncture strength of a separator should be sufficiently high to prevent this from occurring.

The safety of a separator, a distinct characteristic from the above basic characteristics of a battery separator, is quite necessary since this feature allows the battery circuit to be interrupted by the closure of the separator's micropores when a large amount of current flows suddenly, as during an external short circuit.

This battery circuit interruption phenomenon caused by the closure of separator micropores is called 'separator shut down'. Furthermore, the separator's resistance to melt down during a temperature rise after the closure of the micropores is also very important.

Current should become zero after a separator shut down is completed. However, this rarely happens and it is difficult to perform a shut down and control a temperature increase simultaneously since the temperature steadily increases to a certain degree even after the start of a

separator shut down. When a separator loses its shape too early, direct electrode fusion can occur, which is extremely dangerous. Therefore, it is quite important to always maintain the separator shape above the melt temperature.

5 The separator material is a factor influencing separator safety features such as the shut down characteristics and resistance to melt down. Although polyethylene, which has a low melting point, is chiefly used in the current lithium ion batteries since its early shut down feature makes it easy to restrain the temperature increase related to the closure of the micropores, it
10 has a disadvantage of having poor mechanical properties.

However, polyethylene is sometimes used together with polypropylene depending on the desired separator shut down characteristics, resistance to melt down, and mechanical properties.

A method for manufacturing a lithium ion battery separator by
15 laminating polyethylene and polypropylene is disclosed in European Patent Nos. 715,364, 718,901, and 723,304, U.S.A. Patent Nos. 5,240,655, 5,342,695, and 5,472,792, and Japanese Laid-open Patent No. Heisei 4-181651, etc.

However, this method has disadvantages in that it is difficult to make
20 a thin separator, the processing technology is delicate, and the polyethylene layer is easily delaminated from the polypropylene layer due to weak adhesion between the layers.

Additionally, a method for manufacturing a microporous membrane using a polyethylene and polypropylene blend base was introduced in U.S.A.
25 Patent Nos. 5,385,777 and 5,480,745. However, the usefulness of this method is obviously insufficient since this method has not been commercialized, and the associated wettability is also relatively poor.

Methods for manufacturing a porous film using polyolefin are mainly divided into a dry type method and wet type method, from which monoaxial
30 and biaxial methods are known for the stretching processes related to the

formation of numerous micropores.

Although there are many processes that can be used theoretically or in a laboratory, the commercially available microporous films for a separator are those produced with the wet type method using filler or wax and solvent, and those from the dry type method not using a solvent. The wet type method is relatively well known to result in the outstanding puncture strength of the battery separator.

In practice, when microporous films are manufactured using the various types of polyolefin, the resulting shut down initiation temperature of polyethylene is outstanding at 130°C, while the mechanical strength is inferior. On the other hand, polypropylene has outstanding mechanical strength while it exhibits safety problems since the shut down initiation temperature is over 160°C.

SUMMARY OF THE INVENTION

Accordingly, the present invention provides a method for manufacturing a microporous film having outstanding shut down and mechanical characteristics by blending polyolefin and applying the same to a secondary battery separator in order to ameliorate the above problems.

Furthermore, although these polyolefins are blended so as to be manufactured into a microporous film, their wettabilities in a battery electrolyte are low since they are hydrophobic. Therefore, the surface of a microporous film is treated to improve wettability in the present invention.

Additionally, of the methods for manufacturing a porous film, the dry type method out is a simple process in which a solvent is not used. However, the dry type method results in a battery separator with relatively inferior puncture strength. However, the present invention utilizes the dry type method to manufacture a microporous film having outstanding puncture strength.

It is an object of the present invention to provide a microporous film made of polyolefin blend having outstanding electrolyte wettability, puncture

strength, and shut down characteristics, and a method for manufacturing the same, and for applying a microporous film to a secondary battery separator.

It is other object of the present invention to improve shut down characteristics by manufacturing a battery separator with a blend of polyethylene and polypropylene, to improve the wettability of a film of a hydrophobic material by irradiating its surface with ionizing radiation, and to improve the puncture strength of a microporous film manufactured with the dry type method.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 In the following detailed description, only the preferred embodiments of the invention have been shown and described, simply by way of illustration of the best mode contemplated by the inventor(s) of carrying out the invention. As will be realized, the invention is capable of modification in various obvious respects, all without departing from the invention.
15 Accordingly, the description is to be regarded as illustrative in nature, and not restrictive.

The present invention provides a microporous film characterized in that its manufacturing processes comprise the steps of molding a film with a blend containing two or more polyolefins by using a casting or by film blowing,
20 manufacturing a microporous film by annealing or stretching the molded film, and surface treating, i.e., irradiating the film with ionizing radiation before or after the pore formation.

Furthermore, a microporous film manufactured by the above manufacturing method is applied in the present invention to a separator that separates the anode and the cathode of a lithium ion secondary battery or an alkali secondary battery.
25

Polyethylene in the present invention includes low density polyethylene (LDPE), linear low density polyethylene (LLDPE), high density polyethylene (HDPE), etc., wherein the resins have a melt index of from 0.05
30 to 60 g/(10 minutes), and that of polypropylene is from 0.5 to 20 g/(10

minutes).

The mixed blend of the present invention comprises a mixture of polypropylene having a high melting point and polyethylene having a low melting point with a mixed weight ratio ranging from 1:9 to 9:1. Furthermore, 5 an appropriate amount of additives can be put into the mixed blend in order to improve the function of the separator. These additives include antioxidants, plasticizers, flame retardants, colorants, compatibilizers, etc.

The blending of polypropylene, polyethylene, and necessary additives is carried out using appropriate compounding machines such as a 10 banbury or a twin screw extruder, etc.

This obtained mixed blend can be molded into films using the general film molding methods of thermoplastic resins such as casting or film blowing.

Although there is not any special limit for the film molding, a lower 15 processing temperature is preferable, the draw ratio is usually over 20, and the take-up speed is preferably 10 to 100 meters/minute, wherein the draw ratio is a value dividing a winding speed by a linear speed of resins in a die.

The annealing is performed to increase the degree of crystallization and the elasticity recovery ratio to over 50%. The annealing can use a 20 method in which a film is adhered on a heated metal plate, a method in which a film is heated in an oven, a method in which a film is heated by infrared ray irradiation by winding or unwinding a film on a roll inside or outside an oven, or a method in which a roll is double wound with a film such as polyethyleneterephthalate and the roll is heated in an oven, etc. An 25 annealing temperature is set from a temperature that is about 50°C lower than a melting point of a film to the melting point, or can be adjusted by varying the temperature in stages. An annealing time of over 30 seconds is beneficial. When an annealing time is less than 10 seconds, the elasticity recovery ratio increase is insignificant since the annealing of the film is not 30 sufficient.

A film obtained from this annealing process can be manufactured into a microporous film having micropores through a stretching process using the following two methods.

First, after a film is monoaxially or biaxially stretched 10 to 120% of the precursor film while at a temperature in the range of the glass transition temperature of the film to a temperature of 45°C lower than the melting point of polyethylene having the lowest melting point, it is then stretched 50 to 170% of the precursor film while increasing the temperature within the range from a temperature of 45°C lower than the melting point of polyethylene to the melting point temperature of polypropylene.

After the stretching is finished, the temperature is fixed at a value of 5°C or more lower than the melting point of the polypropylene film while the film is maintained in a state under which tension is applied, and may it be contracted up to 5 to 100% of the precursor film.

The film surface treatment is done by irradiation with ionizing radiation either before or after the above annealing process and in the middle or after the stretching process.

The present invention uses ion beams wherein, one or more of the energized ion particles are selected from a group consisting of electrons, hydrogen, oxygen, helium, fluorine, neon, argon, krypton, air, and N₂O.

Furthermore, when the ionizing radiation is irradiated while infusing a reactive gas, one or more of the reactive gases are selected from a group consisting of hydrogen, oxygen, nitrogen, ammonia, carbon monoxide, carbon dioxide, carbon tetrafluoride, methane, and N₂O.

Not only ion beams, but also gamma rays, plasma, electron beams, etc. can be used in the irradiation of the ionizing radiation.

The above mentioned processes describes the total process for manufacturing a separator having the optimum physical properties wherein, part of the steps can be omitted or additional steps can be added according to the desired final physical properties. The following physical properties of

a microporous film manufactured using the above method have been measured:

- 1) Thickness,
- 2) Air permeability: JIS P 8117,
- 5 3) Porosity: American Society for Testing and Materials (ASTM) D2873,
- 4) Pore size: Mercury porosimeter,
- 5) Tensile strength and tensile modulus: ASTM D882,
- 6) Puncture strength,
- 10 7) Shut-down temperature,
- 8) Melting temperature,
- 9) Wettability: a relative ratio of permeation based on a mixture of ethylene carbonate containing 1 mole of LiPF_6 and dimethyl carbonate.

EXAMPLES

EXAMPLE 1

After mixing in a twin screw extruder a blend comprising 70 wt% of polypropylene having a melt index of 2.0 g/(10 minute) and a melting point of 164°C and 30 wt% of polyethylene having a melt index of 3.0 g/(10 minute) and a melting point of 128°C, a precursor film was manufactured using a T-die attached single screw extruder and a winding device. The applied extrusion temperature was 200°C and the draw ratio was 132.

This manufactured precursor film was annealed at a temperature of 110°C in a drying oven for 10 minutes.

The above film was monoaxially stretched achieving a stretching ratio of 60% of the precursor film length at room temperature by the roll stretching method.

After finishing the stretching at room temperature, the film again was stretched to 180% of the precursor film length using an annealing roll at a

temperature of 80°C.

After completing this stretching, heat was applied to the film for 2 minutes while under a state of tension provided by using an annealing roll set at 100°C, and it then was cooled to manufacture a microporous film.

5 After putting this obtained microporous film into a vacuum chamber in which a vacuum of 10^{-5} to 10^{-6} torr was maintained, argon ion particles (Ar^+) were irradiated on both sides of the film by an ion gun. The ion beam energy and ion irradiation amount were 2 keV, and 10^{18} ions/ cm^2 , respectively.

The physical properties of the resulting microporous membrane are
10 represented in Table 1.

EXAMPLE 2

A precursor film was manufactured by the same method as
EXAMPLE 1, and annealing was performed on this precursor film in a drying
15 oven at a temperature of 75°C for 15 minutes.

After surface treating this film by an ion irradiation method having the same condition as in EXAMPLE 1, the film was stretched at a room temperature and a high temperature by a stretching method having the same conditions as in EXAMPLE 1 to obtain a microporous film.

20 The physical properties of the resulting microporous membrane are represented in Table 1.

EXAMPLE 3

After manufacturing a precursor film by the same method as in
25 EXAMPLE 1, this precursor film was put into a vacuum chamber in which a vacuum of 10^{-5} to 10^{-6} torr was maintained, and the film was surface treated by irradiating argon ion particles (Ar^+) on both sides of this film by an ion gun. The ion beam energy and ion irradiation amount were 2 keV, and 10^{12} ions/ cm^2 , respectively.

30 After annealing was performed on this obtained film in a drying oven

for 15 minutes at 75°C as in EXAMPLE 2, the film was stretched at a room temperature and a high temperature by a stretching method having the same conditions as in EXAMPLE 1 to obtain a microporous film.

The physical properties of the resulting microporous membrane are represented in Table 1.

EXAMPLE 4

After mixing a blend comprising 45 wt% of polypropylene having a melt index of 2.0 g/(10 minute) and a melting point of 164°C and 55 wt% of polyethylene having a melt index of 1.0 g/(10 minute) and a melting point of 134°C in a twin screw extruder, a precursor film was manufactured using a T-die attached single screw extruder and winding device. The applied extrusion temperature was 210°C and the draw ratio was 170.

This manufactured precursor film was annealed at a temperature of 90°C in a drying oven for 1 minute.

The above film was monoaxially stretched to a stretching ratio of 30% of the precursor film length at room temperature by the roll stretching method.

After finishing the stretching at room temperature, the film again was stretched to 180% of the precursor film using an annealing roll at a temperature of 100°C.

After completing this stretching, heat was applied to the film for 1 minute under a state of tension provided by using an annealing roll fixed at 100°C, and the film was again contracted 60% of the precursor film length, and cooled in order to manufacture a microporous film.

After putting this obtained microporous film into a vacuum chamber in which a vacuum of 10^{-5} to 10^{-6} torr was maintained, the film was surface treated by infusing a reactive gas of O_2 into and around the film at a rate of 4 mL/min and by irradiating hydrogen ion particles (H_2^+) on both sides of this film with an ion gun. The ion beam energy and ion irradiation amount were

0.3 keV, and 10^{18} ions/cm², respectively.

The physical properties of the resulting microporous membrane are represented in Table 1.

5 EXAMPLE 5

After manufacturing a precursor film by the same method as in EXAMPLE 4, annealing was carried out on this precursor film in a drying oven at a temperature of 80°C for 15 minutes.

After surface treating this film by using an ion irradiating method
10 having the same conditions as in EXAMPLE 4 except for using a reactive gas of CO₂, the film was stretched at room temperature and a high temperature by a stretching method having the same conditions as in EXAMPLE 4 to obtain a microporous film.

The physical properties of the resulting microporous membrane are
15 represented in Table 1.

EXAMPLE 6

After manufacturing a precursor film by the same method as in EXAMPLE 4, this precursor film was put into a vacuum chamber in which a
20 vacuum of 10^{-5} to 10^{-6} torr was maintained, and the film was surface treated by infusing a reactive gas of O₂ into and around the film at a rate of 4 ml/min and irradiating hydrogen ion particles (H₂⁺) on both sides of this film with an ion gun. The ion beam energy and ion irradiation amount were 0.3 keV, and 10^{15} ions/cm², respectively.

25 After annealing was performed on this obtained film in a drying oven for 1 minute at 90°C in conditions as in EXAMPLE 4, the film was stretched at a room temperature and a high temperature by a stretching method having the same conditions as in EXAMPLE 1 to obtain a microporous film.

The physical properties of the resulting microporous membrane are
30 represented in Table 1.

EXAMPLE 7

After mixing a blend comprising 60 wt% of polypropylene having a melt index of 1.0 g/(10 minute) and a melting point of 161°C and 40 wt% of polyethylene having a melt index of 0.5 g/(10 minute) and a melting point of 125°C in a twin screw extruder, a precursor film was manufactured using a T-die attached single screw extruder and winding device. The applied extrusion temperature was 237°C and the draw ratio was 85.

This manufactured precursor film was annealed at a temperature of 120°C in a drying oven for 1 minute.

The above film was monoaxially stretched to a stretching ratio of 55% of the precursor film length at a temperature of 60°C by the roll stretching method.

After finishing the stretching, the film again was stretched to 145% of the precursor film using an annealing roll at a temperature of 110°C.

After completing this stretching, a microporous film was manufactured by cooling the film after applying heat for 5 minutes with 50% of the precursor film contracted under a state of tension given while using an annealing roll set at 150°C.

Gamma (γ) rays were irradiated on this obtained microporous film in an air atmosphere. The dose of irradiation was 1.5 Mrad.

The physical properties of the resulting microporous membrane are represented in Table 1.

COMPARATIVE EXAMPLE 1

After manufacturing a precursor film by the same method as in EXAMPLE 1, annealing was performed on this precursor film in a drying oven at a temperature of 65°C for 10 minutes. This film was stretched at a room temperature and a high temperature by a stretching method having the same conditions as in EXAMPLE 1 to obtain a microporous film.

The physical properties of the resulting microporous membrane are represented in Table 1.

COMPARATIVE EXAMPLE 2

5 After manufacturing a precursor film by the same method as in EXAMPLE 4, annealing was performed on this precursor film in a drying oven at a temperature of 105°C for 1 minute. This film was stretched at a room temperature and a high temperature by a stretching method having the same conditions as in EXAMPLE 4 to obtain a microporous film.

10 The physical properties of the resulting microporous membrane are represented in Table 1.

COMPARATIVE EXAMPLE 3

A precursor film was manufactured with polypropylene having a melt index of 2.0 g/(10 minute) and a melting point of 164°C using a T-die attached single screw extruder and winding device. The applied extrusion temperature was 230°C and the draw ratio was 120.

This manufactured precursor film was annealed at a temperature of 140°C in a drying oven for 3 minutes.

20 This film was monoaxially stretched to a stretching ratio of 70% of the precursor film length at a temperature of 50°C by the roll stretching method.

After finishing the stretching, the film was again stretched to 140% of the precursor film using an annealing roll at a temperature of 130°C.

25 After completing this stretching, heat was applied on the film for 5 minutes under a state of tension given by using an annealing roll set at 150°C, and it was then cooled to manufacture a microporous film.

After putting this obtained microporous film into a vacuum chamber in which a vacuum of 10^{-5} to 10^{-6} torr was maintained, the film was surface
30 treated by irradiating argon ion particles (Ar^+) on both sides of this film with

an ion gun. The ion beam energy and ion irradiation amount were 0.6 keV, and 10^{17} ions/cm², respectively.

The physical properties of the resulting microporous membrane are represented in Table 1.

5

COMPARATIVE EXAMPLE 4

A precursor film was manufactured with polyethylene having a melt index of 3.0 g/(10 minute) and a melting point of 128°C using a T-die attached single screw extruder and winding device. The applied extrusion
10 temperature was 200°C and the draw ratio was 155.

This manufactured precursor film was annealed at a temperature of 100°C in a drying oven for 15 minutes.

This film was monoaxially stretched to a stretching ratio of 30% of the precursor film length at a temperature of 0°C by the roll stretching
15 method.

After finishing the stretching, the film again was stretched to 170% of the precursor film length using an annealing roll at a temperature of 100°C.

After completing this stretching, heat was applied on the film for 5 minutes while it was in a state of tension provided by using an annealing roll
20 set at 110°C, and it was then cooled to manufacture a microporous film.

After putting this obtained microporous film into a vacuum chamber in which a vacuum of 10^{-4} to 10^{-5} torr was maintained, the film was surface treated by infusing a reactive gas of N₂ into and around the film at a rate of 8 ml/min and by irradiating argon ion particles (Ar⁺) on both sides of this film
25 with an ion gun. The ion beam energy and the amount of ion irradiation were 1.0 keV, and 10^{15} ions/cm², respectively.

The physical properties of the resulting microporous membrane are represented in Table 1.

30

Table 1

Classification	EX 1	EX 2	EX 3	EX 4	EX 5	EX 6	EX 7	COM EX 1	COM EX 2	COM EX 3	COM EX 4
Film Thickness(μm)	25	25	25	25	25	25	27	25	25	27	25
Pore size (μm)	0.05	0.04	0.04	0.06	0.05	0.05	0.04	0.04	0.05	0.03	0.07
Porosity (%)	39	36	36	41	37	36	38	36	35	40	44
Air permeability (sec/100cc)	580	670	650	600	750	740	840	660	735	630	490
Puncture strength(g)	460	455	470	430	410	460	510	410	375	480	310
Tensile strength (kgf/cm ²)	1650	1480	1610	1520	1390	1490	1710	1300	1150	1800	1160
Tensile modulus (kgf/cm ²)	9800	9300	9500	8600	8100	8400	11200	8100	6400	10800	8400
Shut-down Temperature (°C)	142	141	142	134	133	135	136	141	134	165	130
Melting Temperature(°C)	176	170	169	164	164	164	172	169	161	168	134
Wettability EC/DMC ratio = 4/6	⊙	⊙	⊙	⊙	⊙	⊙	⊙	△	○	△	○
Wettability EC/DMC ratio = 5/5	⊙	○	○	⊙	○	○	○	X	△	X	△
Wettability EC/DMC ratio = 6/4	○	△	△	⊙	△	△	△	X	X	X	X
Wettability EC/DMC ratio = 7/3	△	X	X	○	X	X	X	X	X	X	X

⊙: wettability is very good;

○: wettability is good;

△: wettability is fair;

5 X: wettability is bad.

A microporous film made of polyolefin blend manufactured by the present invention has outstanding electrolyte wettability, puncture strength, and shut down characteristics, and the thickness of a separator can be
10 further reduced since the film is molded into a single layer by a blend.

Furthermore, secondary batteries in which this microporous film is applied as a separator, especially lithium ion secondary batteries or alkali secondary batteries, are safe due to outstanding puncture strength, shut

down characteristics, and separator melting resistance during large external electric current flows. Furthermore, the manufacture of such batteries can achieve a high degree of productivity during the battery assembly due to the excellent separator electrolyte wettability. Additionally, such microporous
5 film applied as a separator can make high charging density possible due to the thin thickness and high mechanical strength of such a separator.

While the present invention has been described in detail with reference to the preferred embodiments, those skilled in the art will appreciate that various modifications and substitutions can be made thereto
10 without departing from the spirit and scope of the present invention as set forth in the appended claims.

WHAT IS CLAIMED IS:

1. A microporous film manufactured by a process comprising the steps of :

- 5 a) molding a film with a mixed blend containing two or more of polyolefins by using a casting or film blowing;
- b) manufacturing a microporous film by annealing and stretching the molded film; and
- 10 c) treating the surface of film by irradiation with ionizing radiation either before or after the pore formation.

2. A microporous film in accordance with claim 1, wherein the mixed blend comprises two or more of polyolefin mixtures having a melting point difference of over 10°C.

15 3. A microporous film in accordance with claim 1, wherein the mixed blend comprises a mixture in which polypropylene having a high melting point and polyethylene having a low melting point are mixed in a weight ratio ranging from 1:9 to 9:1.

4. A microporous film in accordance with claim 1, wherein the surface treatment of irradiation with ionizing radiation is performed on one side or on both sides of the film.

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5. A microporous film in accordance with claim 1, wherein the surface treatment irradiation with ionizing radiation improves the hydrophilicity and/or mechanical properties of the film by irradiating energized ion particles on the film under a vacuum.

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6. A microporous film in accordance with claim 1, wherein the surface treatment irradiation with ionizing radiation improves the hydrophilicity and/or mechanical properties of the film by the infusion of a reactive gas under a vacuum state by means of irradiating energized ion particles on the film.

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7. A microporous film in accordance with claim 5 or claim 6, wherein one or more of ion particles are selected from a group consisting of electrons, hydrogen, oxygen, helium, fluorine, neon, argon, krypton, air, and N_2O .

5 8. A microporous film in accordance with claim 6, wherein one or more of reactive gases are selected from a group consisting of hydrogen, oxygen, nitrogen, ammonia, carbon monoxide, carbon dioxide, carbon tetrafluoride, methane, and N_2O .

9. A microporous film in accordance with claim 1, wherein the
10 ionizing radiation is selected from a group consisting of ions, gamma (γ) rays, plasma, and electron beams.

10. A method for manufacturing a microporous film manufactured by a process comprising the steps of:

- 15 a) molding a film with a mixed blend containing two or more of polyolefins by using a T-die extruder or film blowing;
- b) manufacturing a microporous film by annealing and stretching the
molded film; and
- c) treating the surface of film by irradiation with ionizing radiation
20 before or after the pore formation.

11. A method for manufacturing a microporous film in accordance with claim 10, wherein the mixed blend comprises two or more of polyolefin mixtures having a melting point difference of over $10^\circ C$.

12. A method for manufacturing a microporous film in
25 accordance with claim 10, wherein the mixed blend comprises a mixture in which polypropylene having a high melting point and polyethylene having a low melting point are mixed in a weight ratio ranging from 1:9 to 9:1.

13. A method for manufacturing a microporous film in accordance with claim 10, wherein the surface treatment of irradiation with
30 ionizing radiation is performed on one side or both sides of the film.

14. A method for manufacturing a microporous film in accordance with claim 10, wherein the surface treatment irradiation with ionizing radiation improves the hydrophilicity and/or mechanical properties of a film by irradiating the film with energized ion particles under a vacuum.

5 15. A method for manufacturing a microporous film in accordance with claim 10, wherein the surface treatment irradiation with ionizing radiation improves the hydrophilicity and/or mechanical properties of a film by the infusion of a reactive gas under a vacuum state by means of the irradiation of the film with energized ion particles .

10 16. A method for manufacturing a microporous film in accordance with claim 14 or claim 15, wherein one or more of ion particles are selected from a group consisting of electrons, hydrogen, oxygen, helium, fluorine, neon, argon, krypton, air, and N₂O.

15 17. A method for manufacturing a microporous film in accordance with claim 15, wherein one or more of reactive gases are selected from a group consisting of hydrogen, oxygen, nitrogen, ammonia, carbon monoxide, carbon dioxide, carbon tetrafluoride, methane, and N₂O.

18. A method for manufacturing a microporous film in accordance with claim 10, wherein the ionizing radiation is selected from a
20 group consisting of ions, gamma (γ) rays, plasma, and electron beams.

19. A lithium ion secondary battery separator or alkali secondary battery separator comprising a microporous film manufactured in accordance with claim 10.

COMBINED DECLARATION AND POWER OF ATTORNEY

(Original, Design, National Stage of PCT, Divisional, Continuation or C-1-P Application)

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

"SAPARATOR FOR SECONDARY BATTERY AND POROUS FILM MADE OF POLYOLEFIN BLEND AND PROCESS FOR PREPARING THE SAME"

This declaration is of the following type:

- ☐ original
- ☐ design
- ☒ national stage of PCT.
- ☐ divisional
- ☐ continuation
- ☐ continuation-in-part (C-I-P)

The specification of which *(complete (a), (b), or (c))*

- ☐ is attached hereto.
- ☐ was filed on as Application Serial No. _____ and was amended on *(if applicable)*
- ☒ was described and claimed in PCT International Application No. PCT/KR99/00750 filed on December 8, 1999 and was amended on *(if applicable)*.

Acknowledgement of Review of Papers and Duty of Candor

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of the subject matter claimed in this application in accordance with Title 37, Code of Federal Regulations § 1.56.

In compliance with this duty there is attached an information disclosure statement. 37 CFR 1.98.

Priority Claim

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT International Application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign applications) for patent or inventor's certificate or any PCT International Application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application on which priority is claimed

(complete (d) or (e))

- (d) ☐ no such applications have been filed.
- (e) ☒ such applications have been filed as follows.

PRIOR FOREIGN/PCT APPLICATION(S) FILED WITHIN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO SAID APPLICATION			
COUNTRY	APPLICATION NO	DATE OF FILING (day, month, year)	DATE OF ISSUE (day, month, year)
Korea	1998-53667	08/12/1998	
			PRIORITY CLAIMED UNDER 35 USC 119 <input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
ALL FOREIGN APPLICATION(S), IF ANY, FILED MORE THAN 12 MONTHS (6 MONTHS FOR DESIGN) PRIOR TO SAID APPLICATION			
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

Claim for Benefit of Prior U.S. Provisional Application(s)

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below

Provisional Application Number	Filing Date

Claim for Benefit of Earlier U.S./PCT Application(s) under 35 U.S.C. 120

Complete this part only if this is a divisional, continuation or C-I-P application

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior application(s) in the manner provided by the first paragraph of Title 35, United States Code § 112, I acknowledge the duty to disclose information as defined in Title 37, Code of Federal Regulations, § 1.56 which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application.

Application Serial No.	December 8, 1999	pending
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)
(Application Serial No.)	(Filing Date)	(Status) (patented, pending, abandoned)

Power of Attorney

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon

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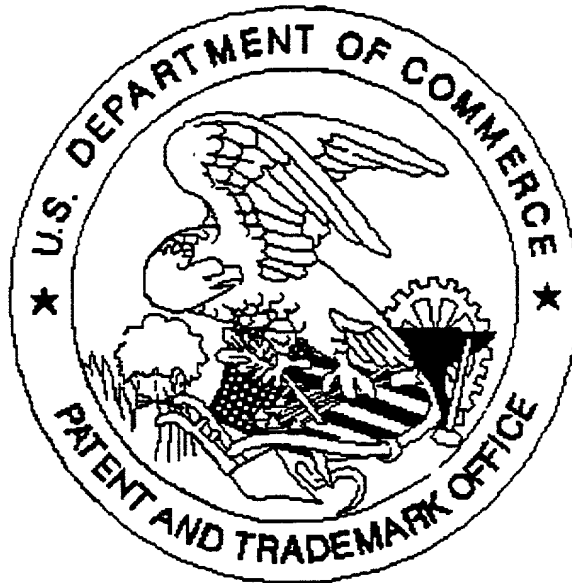
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DATE May 30, 2001	SIGNATURE OF INVENTOR <i>Myung-Man Kim</i>			

Check proper box(es) for any added page(s) forming a part of this declaration

☐ Signature for ninth and subsequent joint inventors. Number of pages added _____

- ☐ Signature by administrator(trix), executor(trix) or legal representative for deceased or incapacitated inventor.
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- ☐ Signature for inventor who refuses to sign, or cannot be reached, by person authorized under 37 CFR 1.47.
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